

## PATENT ABSTRACTS OF JAPAN

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NISHIHARA AKIRA**(54) HYPERFINE PARTICLE LOW RESISTANT TIN DOPE INDIUM OXIDE POWDER AND PRODUCTION THEREOF**

(57)Abstract:

PURPOSE: To provide hyperfine particle low resistant tin dope indium oxide powder and production thereof.

CONSTITUTION: Mixed water solution of indium chloride and tin chloride and ammonium carbonate are mixed to coprecipitate hydroxides of indium and tin at 5-95°C under the conditions that the final pH is 2-8 and the precipitate is heat-decomposed, causing hyperfine particle low resistant tin dope indium oxide powder (ITO powder) having 0.005-0.3 Sn/In composition ratio  $\geq 10\text{m}^2/\text{g}$  specific surface area (BET value),  $\leq 70\Omega\text{cm}$  specific resistance,  $\leq 0.1\%$  impurity chlorine,  $\leq 10\text{ppm}$  impurity sodium and potassium and  $\leq 10\text{ppm}$  free indium and tin. Since the ITO powder is hyperfine particles of  $\leq 0.08\mu\text{m}$  particle diameter, preferably of  $\leq 0.03\mu\text{m}$  and has high conductivity of  $\leq 70\Omega\text{cm}$ , preferably of  $\leq 15\Omega\text{cm}$ , resin or coating material where the powder is dispersed has excellent transparency and conductivity to get resin or a conductive coated film without deterioration with the elapse of time such as discoloration.

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## CLAIMS

[Claim(s)]

[Claim 1] Super-particle low resistance tin dope indium oxide powder whose specific resistance specific surface area (BET value) is below 70-ohmcm more than  $10\text{m}^2/\text{g}$  and whose indium and tin of 10 ppm or less and isolation presentation ratio Sn/In is 0.005-0.3, and 0.1% or less, sodium, and a potassium are 10 ppm or less for the chlorine of an impurity.

[Claim 2] Super-particle low resistance tin dope indium oxide powder of claim 1 whose presentation ratio Sn/In is 0.01-0.1 and whose specific resistance specific surface area (BET value) is below 15-ohmcm more than  $25\text{m}^2/\text{g}$ .

[Claim 3] The manufacture approach of the super-particle low resistance tin dope indium oxide powder which is made to carry out coprecipitation of the hydroxide of an indium and tin by mixing with indium chloride, and the mixed water solution of tin chloride and an ammonium carbonate, and is characterized by decomposing this precipitate thermally.

[Claim 4] The manufacture approach of claim 3 that coprecipitation temperature is 5 degrees C - 95 degrees C, and the last pH of a coprecipitation reaction is 2-8.

[Claim 5] The manufacture approach of claims 3 or 4 that thermal decomposition temperature is 400 degrees C - 950 degrees C, and thermal decomposition time amount is 30 minutes - 8 hours.

## DETAILED DESCRIPTION

### [Detailed Description of the Invention]

[0001]

[Industrial Application] As for this invention, specific surface area (BET value) is preferably related [ a BET value ] with the tin dope indium oxide (ITO) powder and process of the super-particle low resistance whose specific resistance is below 15-ohmcm by specific resistance more than 25m2/g below 70-ohmcm more than 10m2/g. The above-mentioned ITO powder is excellent in dispersibility, and the coating which distributed this powder has the outstanding transparency and conductivity, and can form a paint film stable for a long time.

[0002]

[The conventional technique and a trouble] Conventionally, as a general process of super-particle ITO powder, alkali water solutions, such as a sodium hydroxide and a potassium hydroxide, are added to the mixed water solution of  $\text{InCl}_3$  and  $\text{SnCl}_4$ , coprecipitation of the hydroxide of In and Sn is carried out, and the method of decomposing this precipitate thermally and obtaining the above-mentioned ITO powder is learned. The sodium chloride or potassium chloride which carried out the byproduction at this time is producing commercially the precipitate which repeated washing in cold water frequently with the decantation, the centrifuge method, etc., and was removed and filtered through the process of desiccation, baking, and grinding. The particle size of the above-mentioned powder is adjusted by controlling the above-mentioned reaction temperature and burning temperature. Moreover, since tetravalent  $\text{Sn}^{4+}$  carries out permutation arrangement of the electric conduction device of ITO to the trivalent  $\text{In}^{3+}$  site of  $2\text{OIn}_3$  crystal and it works as a donor of n form, low resistance-ization is performed when the specific resistance of ITO powder adjusts presentation ratio Sn/In within the limits of 0.005-0.3.

[0003] However, there was a limitation in specific resistance (50kg/cm<sup>2</sup> of green compacts) obtaining super-particle ITO powder small enough as the 1st trouble with the conventional ITO powder. That is, by the conventional approach, even if NaCl which carried out the byproduction at the time of precipitate, or KCl is incorporated in the grid of the hydroxide of In and Sn which coprecipitated and fully rinses with a decantation or a centrifuge method, in order that Cl, Na, or K may remain 0.05% or more at least, respectively, it becomes the factor from which this prevents conductivity, and the super-particle ITO powder with specific resistance small enough is not obtained. Especially the chlorine of an impurity serves as  $\text{Cl}^-$  ion, the charge of  $\text{Sn}^{4+}$  ion is taken, and it considers as  $\text{Sn}^{3+}$  ion, and since a carrier electron pair is extinguished, conductivity falls. 1000 degrees C or more in order that these may act as sintering acid, remarkable grain growth takes place at the temperature of 650 degrees C or more, and in order that powder may coarse-grain-ize impurity chlorine, it becomes impossible to obtain the small ultrafine particle ITO powder of specific resistance furthermore, if Na and K live together 0.1% or more simultaneously although it can be made to \*\*\*\* compulsorily at an elevated temperature. In order that anion  $\text{Cl}^-$  to contain may mainly form cation  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{In}^{3+}$  and  $\text{Sn}^{4+}$ , and ionic bond as the 2nd trouble, When this powder was mixed to resin, and it considered as a Plastic solid or coating-ized, there was a trouble which  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{In}^{3+}$ ,  $\text{Sn}^{4+}$ , and  $\text{Cl}^-$  are eluted, and is easy to cause aging, such as discoloration of resin, cloudiness, and degradation, in the interior of a Plastic solid and a paint film.

[0004] Solution technical-problem] this invention of [invention solves the above-mentioned trouble in the conventional ITO powder, and particle size is a particle 0.03 micrometers or less preferably, and aims 0.08 micrometers or less at specific resistance offering the ultrafine particle ITO powder which was preferably excellent in the conductivity below 15-ohmcm, and its process below 70-ohmcm.

[0005]

The solution means of [problem: Configuration] of invention According to this invention, presentation ratio Sn/In is 0.005-0.3, specific surface area (BET value) is [ specific resistance ] below 70-ohmcm more than 10m<sup>2</sup>/g, and the super-particle low resistance tin dope indium oxide powder whose indium and tin of 10 ppm or less and isolation 0.1% or less, sodium, and a potassium are 10 ppm or less for the chlorine of an impurity is offered. Moreover, according to this invention, coprecipitation of the hydroxide of an indium and tin is carried out by mixing with indium chloride, and the mixed water solution of tin chloride and an ammonium carbonate, and the manufacture approach of the super-particle low resistance tin dope indium oxide powder characterized by decomposing this precipitate thermally is offered.

[0006] The ITO powder of this invention carries out coprecipitation of the hydroxide of an indium and tin by mixing with indium chloride, and the mixed water solution of tin chloride and an ammonium carbonate, and is obtained by decomposing this precipitate thermally. By dropping the mixed water solution of indium chloride InCl<sub>3</sub> and tin chloride SnCl<sub>4</sub> into the water solutions of the ammonium carbonate 3, i.e., ammonium-carbonate (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, ammonium bicarbonate NH<sub>4</sub>HCO<sub>3</sub>, and ammonium carbamate H<sub>2</sub>NCO<sub>2</sub>NH<sub>4</sub>, or these mixed water solutions, coprecipitation of the hydroxide of an indium and tin is carried out, and, specifically, it is obtained by rinsing and grinding [ dry, calcinate and ] this sediment with a decantation or a centrifuge method.

[0007] InCl<sub>3</sub> water solution and SnCl<sub>4</sub> water solution which are used for this invention can use a commercial item. What is necessary is just InCl<sub>3</sub> common water solution and SnCl<sub>4</sub> water solution. In addition, InCl<sub>3</sub> water solution may use what dissolved in 12 N-HCl and the 220 - 280 weight section, and obtained Metal In and the 100 weight sections. InCl<sub>3</sub> water solution and SnCl<sub>4</sub> water solution are mixed so that presentation ratio Sn/Cl in powder may be set to 0.005-0.3. concrete – the InCl<sub>3</sub>, 100 weight section – receiving – SnCl<sub>4</sub> 4 and 1 - 10 weight sections – it is preferably adjusted to the range of 3 - 8 weight section. The specific resistance of the ITO powder obtained when it separated from this range becomes high.

[0008] As a carbonate, ammonium-carbonate (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, ammonium bicarbonate NH<sub>4</sub>HCO<sub>3</sub>, H<sub>2</sub>NCO<sub>2</sub>NH(s)<sub>4</sub>, or such mixture are used. these carbonates -- InCl<sub>3</sub>-SnCl<sub>4</sub> – receiving – the equivalent to the 2.5 time equivalent – using it – last 2-pH 8 – it is preferably adjusted to the range of 3-6. Moreover, HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, CH<sub>3</sub>COOH, or these mixed acids may adjust adjustment of Last pH in predetermined pH range. It is not desirable in order that a precipitate particle may remelt, when Last pH is lower than 2. Moreover, since desorption of carbon dioxide gas is not performed but super-atomization and dechlorination become impossible in case precipitate is calcinated, since the carbonic acid root in precipitate dissolves as HCO<sub>3</sub><sup>-</sup> or CO<sub>3</sub><sup>2-</sup> of an anion when pH exceeds 8, it is not desirable. By using the above-mentioned carbonate, by making precipitate containing the carbonate in which OH<sup>-</sup> in the hydroxide grid of In and Sn which coprecipitated carried out permutation arrangement by HCO<sub>3</sub><sup>-</sup> or CO<sub>3</sub><sup>2-</sup> selectively form, atomization is attained by desorption of carbon dioxide gas at the time of baking, and in this invention, since specific surface area becomes large, dechlorination becomes easy.

[0009] The temperature of a coprecipitation reaction is within the limits of 5 to 95 degrees C, and is within the limits of 10 to 90 degrees C preferably. When temperature is lower than this, the nucleation of precipitate is inadequate, and yield also falls. On the other hand, since carbonic acid decomposes and carbonation is not fully performed when reaction temperature is higher than this range, it is not desirable. In addition, after making precipitate generate at low temperature, you may raise to the above-mentioned reaction temperature range.

[0010] Sediment generated by the above-mentioned approach is rinsed by general cleaning methods, such as a decantation or a centrifuge method, after recovery. Washing is performed until the conductivity of filtrate becomes eventually more than 2000-ohmcm, but it is washed until it becomes preferably more than 5000-ohmcm. Since NH<sub>4</sub>Cl which carried out the byproduction is not removed enough, Cl content after baking is set to 100 ppm or more and a result in which In<sup>3+</sup> and Sn<sup>4+</sup> 10 ppm or more of elution nature are contained, respectively is brought when

the conductivity of precipitate is smaller than this, it is difficult to obtain the ITO powder which has stable physical properties.

[0011] Thermal decomposition is calcinated within the limits of 8 hours from 30 minutes within the limits of 400 to 950 degrees C, and is preferably calcinated within the limits of 1 to 6 hours within the limits of 500 to 850 degrees C. Since it becomes imperfect insufficiently dechlorinating crystallization of ITO when burning temperature is lower than this range, specific resistance becomes large and is not more desirable than 15-ohmcm. Moreover, since a particle coarse-grain-izes, specific surface area (BET value) becomes smaller than 10m<sup>2</sup>/g and particle size is set to about 0.08 micrometers or more when burning temperature is higher than this range, it is difficult to obtain ultrafine particle ITO fine particles. When burning temperature is 500 degrees C - 850 degrees C, the specific surface area (BET value) of a particle becomes more than 25m<sup>2</sup>/g, and ultrafine particle ITO powder about 0.03 micrometers or less is obtained for particle size.

[0012] They are SnCl<sub>4</sub> and 33g of 60wt% water solutions to this indium chloride solution after adding example 1 In metal 200g to 12 N-HCl and 600 cc and dissolving it thoroughly. In addition, InCl<sub>3</sub>-SnCl<sub>4</sub> (Sn/In ratio: 0.05) mixed solution was prepared. Next, 500g NH<sub>4</sub>HCO<sub>3</sub> is dissolved in ion exchange water, and it is 4.5l. of volume. It adjusted to the temperature of 30 degrees C. It was dropped stirring the whole quantity of the InCl<sub>3</sub>-SnCl<sub>4</sub> above-mentioned liquid for about 20 minutes in this water solution, precipitate was made to generate, and it stirred for 30 minutes further as it is. At this time, the last pH of reaction mixture was 4.5. Precipitate was collected, centrifugal filtration was performed, adding and washing ion exchange water, after dehydrating with a centrifugal separator, and centrifugal filtration was ended in the place which the conductivity of filtrate arrived at more than 5000-ohmcm. Subsequently, after drying this precipitate at 100 degrees C overnight, at 600 degrees C, it calcinated for 3 hours, it ground, and 213g of ITO powder was obtained. The specific surface area of this powder is 38.8m<sup>2</sup>/g, the first [ an average of ] particle size is 0.023 micrometers, and specific resistance (green compact 50 kg/cm<sup>2</sup>) is 1.8. It was ohmcm. When distilled water was made to distribute 1.0g of this powder, supersonic vibration was given for 20 minutes and the leached moiety was analyzed, it is Cl:13ppm, In:8ppm, and less than [ Sn:1ppm ], and Na and K were not detected. Next, this ITO After having used the heat roll for vinyl chloride resin, kneading 2g of powder by 130 \*\* and pressing it in 0.3mm, when aging of the color under a high-humidity/temperature environment was examined by leaving it for 20 days under conditions with a% [ of humidity ] of 80, and a temperature of 60 degrees C, it was checked that the color of resin changes at all and is stable. Moreover, what mixed 12g of this ITO powder in 40g (10% of resin solid content) of polyester coatings was put into the container, and it stirred for 20 hours using alumina-balls 100g of 10mmphi. After having used the wire bar, applying to polyester film with a thickness of 75 micrometers and seasoning naturally to it after that, it dried for 5 hours and 90 degrees C of paint films with a thickness of 1.2 micrometers were formed. The haze value of this paint film was 8.8%, and surface electrical resistance was 7.6x10<sup>3</sup>ohm/\*\*.

[0013] SnCl<sub>4</sub> and 200g of 60wt% water solutions were added to InCl<sub>3</sub> solution prepared like example 2 example 1, and InCl<sub>3</sub>-SnCl<sub>4</sub> (Sn/In ratio: 0.3) mixed solution was prepared. On the other hand, 550g 2(NH<sub>4</sub>) CO<sub>3</sub> was dissolved in ion exchange water, and it adjusted to volume of 9l., and the temperature of 5 degrees C. It was dropped for about 10 minutes, stirring the whole quantity of the InCl<sub>3</sub>-SnCl<sub>4</sub> above-mentioned liquid in this water solution, the hydrochloric acid was added further, and Last pH was adjusted to 2.0. It ground, after having collected, filtering and drying and calcinating precipitate at 400 degrees C for 8 hours like [ after carrying out temperature up of this mixed solution to 95 degrees C and riping for 30 minutes ] an example 1, and 194g of ITO powder was obtained. The specific surface area of this powder was 72.3m<sup>2</sup>/g, the first [ an average of ] particle size was 0.012 micrometers, and specific resistance (green compact 50 kg/cm<sup>2</sup>) was 15-ohmcm. Moreover, the results of the ultrasonic elution test of this powder are Cl:44ppm, In:7ppm, and less than [ Sn:1ppm ], and Na and K were not detected. The color of resin changes at all and was stable, when the high-humidity/temperature trial was performed after kneading and pressing in vinyl resin on the same conditions as an example 1 using this ITO powder. Moreover, the paint film with a thickness of 1.4 micrometers was formed with the coating prepared on the same conditions as an example 1 using this ITO powder. The haze value of this paint film was 8.0%, and surface electrical resistance was 9.1x10<sup>3</sup>ohm/\*\*.

[0014]  $\text{SnCl}_4$  and 66g of 60wt% water solutions were added to  $\text{InCl}_3$  solution prepared like example 3 example 1, and  $\text{InCl}_3\text{-SnCl}_4$  (Sn/In ratio: 0.10) mixed solution was prepared. On the other hand, 1400g  $\text{NH}_4\text{HCO}_3$  was dissolved in ion exchange water, and it adjusted to volume of 9l., and the temperature of 95 degrees C. It is dropped for about 10 minutes, stirring the whole quantity of the  $\text{InCl}_3\text{-SnCl}_4$  above-mentioned liquid in this water solution, dilute hydrochloric acid is added further, and it is Last pH 6.0 It adjusted. Then, it ground, after having collected, filtering and drying and calcinating precipitate for 30 minutes at 950 degrees C like an example 1, and 217g of ITO powder was obtained. The specific surface area of this powder was  $25.6\text{m}^2/\text{g}$ , the first [ an average of ] particle size was 0.029 micrometers, and specific resistance (green compact 50 kg/cm<sup>2</sup>) was 1.3-ohmcm. Moreover, the result of the ultrasonic elution test of this powder is Cl:6ppm, In and Sn are 1 ppm or less, and Na and K were not detected. The color of resin changes at all and was stable, when the high-humidity/temperature trial was performed after kneading and pressing in vinyl resin on the same conditions as an example 1 using this ITO powder. Moreover, the paint film with a thickness of 1.2 micrometers was formed with the coating prepared on the same conditions as an example 1 using this ITO powder. The haze value of this paint film was 9.4%, and surface electrical resistance was  $7.4 \times 10^3 \text{ohm}/\text{cm}^2$ .

[0015]  $\text{SnCl}_4$  and 3.3g of 60wt% water solutions were added to  $\text{InCl}_3$  solution prepared like example 4 example 1, and  $\text{InCl}_3\text{-SnCl}_4$  (Sn/In ratio: 0.005) mixed solution was prepared. On the other hand, 1400g  $\text{NH}_4\text{HCO}_3$  was dissolved in ion exchange water, and it adjusted to volume of 9l., and the temperature of 95 degrees C. It is dropped for about 10 minutes, stirring the whole quantity of the  $\text{InCl}_3\text{-SnCl}_4$  above-mentioned liquid in this water solution, dilute hydrochloric acid is added further, and it is Last pH 8.0 It adjusted. Then, it ground, after having collected, filtering and drying and calcinating precipitate for 30 minutes at 600 degrees C like an example 1, and 230g of ITO powder was obtained. The specific surface area of this powder was  $25.6\text{m}^2/\text{g}$ , the first [ an average of ] particle size was 0.029 micrometers, and specific resistance (green compact 50 kg/cm<sup>2</sup>) was 60-ohmcm. moreover, the result of the ultrasonic elution test of this powder – Cl:390ppm, In:9ppm, and Sn:7ppm it is – Na and K were not detected. This ITO The color of resin changes at all and was stable, when the high-humidity/temperature trial was performed after kneading and pressing in vinyl resin on the same conditions as an example 1 using powder. Moreover, the paint film with a thickness of 1.2 micrometers was formed with the coating prepared on the same conditions as an example 1 using this ITO powder. The haze value of this paint film was 9.4%, and surface electrical resistance was  $2.1 \times 10^4 \text{ohm}/\text{cm}^2$ .

[0016] They are NaOH and 250g about example of comparison 1  $\text{NH}_4\text{HCO}_3$ . The coprecipitation reaction was carried out like the example 1 except having changed. the last pH at this time – 7.4 it was . Precipitate was succeedingly washed like the example 1, it dried and calcinated, and 220g of ITO powder was obtained. The specific surface area of this powder was  $28.1\text{m}^2/\text{g}$ , the first [ an average of ] particle size was 0.029 micrometers, and specific resistance (green compact 50 kg/cm<sup>2</sup>) was 100-ohmcm. Moreover, the result of the ultrasonic elution test of this powder was Cl:0.2wt% and In:0.05wt% and Sn:0.01wt%, and Na was 0.1wt(s)%. After kneading and pressing in vinyl resin on the same conditions as an example 1 using this ITO powder, when the high-humidity/temperature trial was performed, the color of resin was discolored a little green. Moreover, the paint film with a thickness of 1.4 micrometers was formed with the coating prepared on the same conditions as an example 1 using this ITO powder. The haze value of this paint film was 14.6%, and surface electrical resistance was  $9.7 \times 10^4 \text{ohm}/\text{cm}^2$ .

[0017] They are NaOH and 250g about example of comparison 2  $\text{NH}_4\text{HCO}_3$ . The coprecipitation reaction was carried out like the example 1 except having changed. The last pH at this time was 7.4. Then, precipitate was washed like the example 1, after desiccation, it calcinated at 950 degrees C and 220g of ITO powder was obtained. The specific surface area of this powder was  $4\text{cm}^2/\text{g}$ , the first [ an average of ] particle size was 0.25 micrometers, and specific resistance (green compact 50 kg/cm<sup>2</sup>) was 10-ohmcm. Moreover, the result of the ultrasonic elution test of this powder was Cl:0.12wt% and In:0.05wt% and Sn:0.01wt%, and Na was 0.1wt(s)%. When the high-humidity/temperature trial was performed after kneading and pressing in vinyl resin on the same conditions as an example 1 using this ITO powder, the color of resin was discolored a little green. Moreover, the paint film with a thickness of 1.4 micrometers was formed with the coating prepared on the same conditions as an example 1 using

this ITO powder. The haze value of this paint film was 22.3%, and surface electrical resistance was  $9.7 \times 10^3 \text{ ohm}/\text{cm}^2$ .

[0018]

[Effect of the Invention] Specific surface area (BET value) has the transparency and conductivity the resin with which the ITO powder of this invention is below  $15\text{-ohmcm}$  more than  $25\text{m}^2/\text{g}$  preferably below  $70\text{-ohmcm}$  more than  $10\text{m}^2/\text{g}$ , and specific surface area (BET value) distributed [ specific resistance ] this powder, and a coating excelled [ conductivity ] in specific resistance, and resin without aging, such as discoloration, and a conductive paint film are obtained.

## TECHNICAL FIELD

[Industrial Application] As for this invention, specific surface area (BET value) is preferably related [ a BET value ] with the tin dope indium oxide (ITO) powder and process of the super-particle low resistance whose specific resistance is below  $15\text{-ohmcm}$  by specific resistance more than  $25\text{m}^2/\text{g}$  below  $70\text{-ohmcm}$  more than  $10\text{m}^2/\text{g}$ . The above-mentioned ITO powder is excellent in dispersibility, and the coating which distributed this powder has the outstanding transparency and conductivity, and can form a paint film stable for a long time.

## EFFECT OF THE INVENTION

[Effect of the Invention] Specific surface area (BET value) has the transparency and conductivity the resin with which the ITO powder of this invention is below  $15\text{-ohmcm}$  more than  $25\text{m}^2/\text{g}$  preferably below  $70\text{-ohmcm}$  more than  $10\text{m}^2/\text{g}$ , and specific surface area (BET value) distributed [ specific resistance ] this powder, and a coating excelled [ conductivity ] in specific resistance, and resin without aging, such as discoloration, and a conductive paint film are obtained.

## TECHNICAL PROBLEM

[The conventional technique and a trouble] Conventionally, as a general process of super-particle ITO powder, alkali water solutions, such as a sodium hydroxide and a potassium hydroxide, are added to the mixed water solution of  $\text{InCl}_3$  and  $\text{SnCl}_4$ , coprecipitation of the hydroxide of In and Sn is carried out, and the method of decomposing this precipitate thermally and obtaining the above-mentioned ITO powder is learned. The sodium chloride or potassium chloride which carried out the byproduction at this time is producing commercially the precipitate which repeated washing in cold water frequently with the decantation, the centrifuge method, etc., and was removed and filtered through the process of desiccation, baking, and grinding. The particle size of the above-mentioned powder is adjusted by controlling the above-mentioned reaction temperature and burning temperature. Moreover, since tetravalent  $\text{Sn}^{4+}$  carries out permutation arrangement of the electric conduction device of ITO to the trivalent  $\text{In}^{3+}$  site of  $2\text{OIn}_3$  crystal and it works as a donor of n form, low resistance-ization is performed when the specific resistance of ITO powder adjusts presentation ratio  $\text{Sn}/\text{In}$  within the limits of 0.005-0.3.

[0003] However, there was a limitation in specific resistance ( $50\text{kg}/\text{cm}^2$  of green compacts) obtaining super-particle ITO powder small enough as the 1st trouble with the conventional ITO powder. That is, by the conventional approach, even if  $\text{NaCl}$  which carried out the byproduction at the time of precipitate, or  $\text{KCl}$  is incorporated in the grid of the hydroxide of In and Sn which coprecipitated and fully rinses with a decantation or a centrifuge method, in order that Cl, Na, or K may remain 0.05% or more at least, respectively, it becomes the factor from which this prevents conductivity, and the super-particle ITO powder with specific resistance small enough is not obtained. Especially the chlorine of an impurity serves as  $\text{Cl}^-$  ion, the charge of  $\text{Sn}^{4+}$  ion is taken, and it considers as  $\text{Sn}^{3+}$  ion, and since a carrier electron pair is extinguished, conductivity falls. 1000 degrees C or more in order that these may

act as sintering acid, remarkable grain growth takes place at the temperature of 650 degrees C or more, and in order that powder may coarse-grain-size impurity chlorine, it becomes impossible to obtain the small ultrafine particle ITO powder of specific resistance furthermore, if Na and K live together 0.1% or more simultaneously although it can be made to \*\*\*\* compulsorily at an elevated temperature. In order that anion Cl<sup>-</sup> to contain may mainly form cation Na<sup>+</sup>, K<sup>+</sup>, In<sup>3+</sup> and Sn<sup>4+</sup>, and ionic bond as the 2nd trouble, When this powder was mixed to resin, and it considered as a Plastic solid or coating-ized, there was a trouble which Na<sup>+</sup>, K<sup>+</sup>, In<sup>3+</sup>, Sn<sup>4+</sup>, and Cl<sup>-</sup> are eluted, and is easy to cause aging, such as discoloration of resin, cloudiness, and degradation, in the interior of a Plastic solid and a paint film.

[0004] Solution technical-problem] this invention of [invention solves the above-mentioned trouble in the conventional ITO powder, and particle size is a particle 0.03 micrometers or less preferably, and aims 0.08 micrometers or less at specific resistance offering the ultrafine particle ITO powder which was preferably excellent in the conductivity below 15-ohmcm, and its process below 70-ohmcm.

[0005]

The solution means of [problem: Configuration] of invention According to this invention, presentation ratio Sn/In is 0.005-0.3, specific surface area (BET value) is [ specific resistance ] below 70-ohmcm more than 10m<sup>2</sup>/g, and the super-particle low resistance tin dope indium oxide powder whose indium and tin of 10 ppm or less and isolation 0.1% or less, sodium, and a potassium are 10 ppm or less for the chlorine of an impurity is offered. Moreover, according to this invention, coprecipitation of the hydroxide of an indium and tin is carried out by mixing with indium chloride, and the mixed water solution of tin chloride and an ammonium carbonate, and the manufacture approach of the super-particle low resistance tin dope indium oxide powder characterized by decomposing this precipitate thermally is offered.

[0006] The ITO powder of this invention carries out coprecipitation of the hydroxide of an indium and tin by mixing with indium chloride, and the mixed water solution of tin chloride and an ammonium carbonate, and is obtained by decomposing this precipitate thermally. By dropping the mixed water solution of indium chloride InCl<sub>3</sub> and tin chloride SnCl<sub>4</sub> into the water solutions of the ammonium carbonate 3, i.e., ammonium-carbonate (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, ammonium bicarbonate NH<sub>4</sub>HCO<sub>3</sub>, and ammonium carbamate H<sub>2</sub>NCO<sub>2</sub>NH<sub>4</sub>, or these mixed water solutions, coprecipitation of the hydroxide of an indium and tin is carried out, and, specifically, it is obtained by rinsing and grinding [ dry, calcinate and ] this sediment with a decantation or a centrifuge method.

[0007] InCl<sub>3</sub> water solution and SnCl<sub>4</sub> water solution which are used for this invention can use a commercial item. What is necessary is just InCl<sub>3</sub> common water solution and SnCl<sub>4</sub> water solution. In addition, InCl<sub>3</sub> water solution may use what dissolved in 12 N-HCl and the 220 - 280 weight section, and obtained Metal In and the 100 weight sections. InCl<sub>3</sub> water solution and SnCl<sub>4</sub> water solution are mixed so that presentation ratio Sn/Cl in powder may be set to 0.005-0.3. concrete – the InCl<sub>3</sub>, 100 weight section – receiving – SnCl<sub>4</sub> 4 and 1 - 10 weight sections – it is preferably adjusted to the range of 3 - 8 weight section. The specific resistance of the ITO powder obtained when it separated from this range becomes high.

[0008] As a carbonate, ammonium-carbonate (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, ammonium bicarbonate NH<sub>4</sub>HCO<sub>3</sub>, H<sub>2</sub>NCO<sub>2</sub>NH(s)<sub>4</sub>, or such mixture are used. these carbonates -- InCl<sub>3</sub>-SnCl<sub>4</sub> -- receiving -- the equivalent to the 2.5 time equivalent -- using it -- last 2-pH 8 -- it is preferably adjusted to the range of 3-6. Moreover, HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, CH<sub>3</sub>COOH, or these mixed acids may adjust adjustment of Last pH in predetermined pH range. It is not desirable in order that a precipitate particle may remelt, when Last pH is lower than 2. Moreover, since desorption of carbon dioxide gas is not performed but super-atomization and dechlorination become impossible in case precipitate is calcinated, since the carbonic acid root in precipitate dissolves as HCO<sub>3</sub><sup>-</sup> or CO<sub>3</sub><sup>2-</sup> of an anion when pH exceeds 8, it is not desirable. By using the above-mentioned carbonate, by making precipitate containing the carbonate in which OH<sup>-</sup> in the hydroxide grid of In and Sn which coprecipitated carried out permutation arrangement by HCO<sub>3</sub><sup>-</sup> or CO<sub>3</sub><sup>2-</sup> selectively form, atomization is attained by desorption of carbon dioxide gas at the time of baking, and in this invention, since specific surface area becomes large, dechlorination becomes easy.

[0009] The temperature of a coprecipitation reaction is within the limits of 5 to 95 degrees C, and is within the limits of 10 to 90 degrees C preferably. When temperature is lower than this, the nucleation of precipitate is inadequate,

and yield also falls. On the other hand, since carbonic acid decomposes and carbonation is not fully performed when reaction temperature is higher than this range, it is not desirable. In addition, after making precipitate generate at low temperature, you may raise to the above-mentioned reaction temperature range.

[0010] Sediment generated by the above-mentioned approach is rinsed by general cleaning methods, such as a decantation or a centrifuge method, after recovery. Washing is performed until the conductivity of filtrate becomes eventually more than 2000-ohmcm, but it is washed until it becomes preferably more than 5000-ohmcm. Since  $\text{NH}_4\text{Cl}$  which carried out the byproduction is not removed enough, Cl content after baking is set to 100 ppm or more and a result in which  $\text{In}^{3+}$  and  $\text{Sn}^{4+}$  10 ppm or more of elution nature are contained, respectively is brought when the conductivity of precipitate is smaller than this, it is difficult to obtain the ITO powder which has stable physical properties.

[0011] Thermal decomposition is calcinated within the limits of 8 hours from 30 minutes within the limits of 400 to 950 degrees C, and is preferably calcinated within the limits of 1 to 6 hours within the limits of 500 to 850 degrees C. Since it becomes imperfect insufficiently dechlorinating crystallization of ITO when burning temperature is lower than this range, specific resistance becomes large and is not more desirable than 15-ohmcm. Moreover, since a particle coarse-grain-izes, specific surface area (BET value) becomes smaller than  $10\text{m}^2/\text{g}$  and particle size is set to about 0.08 micrometers or more when burning temperature is higher than this range, it is difficult to obtain ultrafine particle ITO fine particles. When burning temperature is 500 degrees C - 850 degrees C, the specific surface area (BET value) of a particle becomes more than  $25\text{m}^2/\text{g}$ , and ultrafine particle ITO powder about 0.03 micrometers or less is obtained for particle size.

[0012] They are  $\text{SnCl}_4$  and 33g of 60wt% water solutions to this indium chloride solution after adding example 1 In metal 200g to 12 N-HCl and 600 cc and dissolving it thoroughly. In addition,  $\text{InCl}_3\text{-SnCl}_4$  (Sn/In ratio: 0.05) mixed solution was prepared. Next, 500g  $\text{NH}_4\text{HCO}_3$  is dissolved in ion exchange water, and it is 4.5l. of volume. It adjusted to the temperature of 30 degrees C. It was dropped stirring the whole quantity of the  $\text{InCl}_3\text{-SnCl}_4$  above-mentioned liquid for about 20 minutes in this water solution, precipitate was made to generate, and it stirred for 30 minutes further as it is. At this time, the last pH of reaction mixture was 4.5. Precipitate was collected, centrifugal filtration was performed, adding and washing ion exchange water, after dehydrating with a centrifugal separator, and centrifugal filtration was ended in the place which the conductivity of filtrate arrived at more than 5000-ohmcm. Subsequently, after drying this precipitate at 100 degrees C overnight, at 600 degrees C, it calcinated for 3 hours, it ground, and 213g of ITO powder was obtained. The specific surface area of this powder is  $38.8\text{m}^2/\text{g}$ , the first [ an average of ] particle size is 0.023 micrometers, and specific resistance (green compact 50 kg/cm<sup>2</sup>) is 1.8. It was ohmcm. When distilled water was made to distribute 1.0g of this powder, supersonic vibration was given for 20 minutes and the leached moiety was analyzed, it is Cl:13ppm, In:8ppm, and less than [ Sn:1ppm ], and Na and K were not detected. Next, this ITO After having used the heat roll for vinyl chloride resin, kneading 2g of powder by 130 \*\* and pressing it in 0.3mm, when aging of the color under a high-humidity/temperature environment was examined by leaving it for 20 days under conditions with a% [ of humidity ] of 80, and a temperature of 60 degrees C, it was checked that the color of resin changes at all and is stable. Moreover, what mixed 12g of this ITO powder in 40g (10% of resin solid content) of polyester coatings was put into the container, and it stirred for 20 hours using alumina-balls 100g of 10mmphi. After having used the wire bar, applying to polyester film with a thickness of 75 micrometers and seasoning naturally to it after that, it dried for 5 hours and 90 degrees C of paint films with a thickness of 1.2 micrometers were formed. The haze value of this paint film was 8.8%, and surface electrical resistance was  $7.6 \times 10^3 \text{ohm}/**$ .

[0013]  $\text{SnCl}_4$  and 200g of 60wt% water solutions were added to  $\text{InCl}_3$  solution prepared like example 2 example 1, and  $\text{InCl}_3\text{-SnCl}_4$  (Sn/In ratio: 0.3) mixed solution was prepared. On the other hand, 550g  $2(\text{NH}_4) \text{CO}_3$  was dissolved in ion exchange water, and it adjusted to volume of 9l., and the temperature of 5 degrees C. It was dropped for about 10 minutes, stirring the whole quantity of the  $\text{InCl}_3\text{-SnCl}_4$  above-mentioned liquid in this water solution, the hydrochloric acid was added further, and Last pH was adjusted to 2.0. It ground, after having collected, filtering and drying and calcinating precipitate at 400 degrees C for 8 hours like [ after carrying out temperature up of this mixed solution to 95 degrees C and riping for 30 minutes ] an example 1, and 194g of ITO powder was obtained.



The specific surface area of this powder was 72.3m<sup>2</sup>/g, the first [ an average of ] particle size was 0.012 micrometers, and specific resistance (green compact 50 kg/cm<sup>2</sup>) was 15-ohmcm. Moreover, the results of the ultrasonic elution test of this powder are Cl:44ppm, In:7ppm, and less than [ Sn:1ppm ], and Na and K were not detected. The color of resin changes at all and was stable, when the high-humidity/temperature trial was performed after kneading and pressing in vinyl resin on the same conditions as an example 1 using this ITO powder. Moreover, the paint film with a thickness of 1.4 micrometers was formed with the coating prepared on the same conditions as an example 1 using this ITO powder. The haze value of this paint film was 8.0%, and surface electrical resistance was 9.1x10<sup>3</sup>ohm/\*\*.

[0014] SnCl<sub>4</sub> and 66g of 60wt% water solutions were added to InCl<sub>3</sub> solution prepared like example 3 example 1, and InCl<sub>3</sub>-SnCl<sub>4</sub> (Sn/In ratio: 0.10) mixed solution was prepared. On the other hand, 1400g NH<sub>4</sub>HCO<sub>3</sub> was dissolved in ion exchange water, and it adjusted to volume of 9l., and the temperature of 95 degrees C. It is dropped for about 10 minutes, stirring the whole quantity of the InCl<sub>3</sub>-SnCl<sub>4</sub> above-mentioned liquid in this water solution, dilute hydrochloric acid is added further, and it is Last pH 6.0 It adjusted. Then, it ground, after having collected, filtering and drying and calcinating precipitate for 30 minutes at 950 degrees C like an example 1, and 217g of ITO powder was obtained. The specific surface area of this powder was 25.6m<sup>2</sup>/g, the first [ an average of ] particle size was 0.029 micrometers, and specific resistance (green compact 50 kg/cm<sup>2</sup>) was 1.3-ohmcm. Moreover, the result of the ultrasonic elution test of this powder is Cl:6ppm, In and Sn are 1 ppm or less, and Na and K were not detected. The color of resin changes at all and was stable, when the high-humidity/temperature trial was performed after kneading and pressing in vinyl resin on the same conditions as an example 1 using this ITO powder. Moreover, the paint film with a thickness of 1.2 micrometers was formed with the coating prepared on the same conditions as an example 1 using this ITO powder. The haze value of this paint film was 9.4%, and surface electrical resistance was 7.4x10<sup>3</sup>ohm/\*\*.

[0015] SnCl<sub>4</sub> and 3.3g of 60wt% water solutions were added to InCl<sub>3</sub> solution prepared like example 4 example 1, and InCl<sub>3</sub>-SnCl<sub>4</sub> (Sn/In ratio: 0.005) mixed solution was prepared. On the other hand, 1400g NH<sub>4</sub>HCO<sub>3</sub> was dissolved in ion exchange water, and it adjusted to volume of 9l., and the temperature of 95 degrees C. It is dropped for about 10 minutes, stirring the whole quantity of the InCl<sub>3</sub>-SnCl<sub>4</sub> above-mentioned liquid in this water solution, dilute hydrochloric acid is added further, and it is Last pH 8.0 It adjusted. Then, it ground, after having collected, filtering and drying and calcinating precipitate for 30 minutes at 600 degrees C like an example 1, and 230g of ITO powder was obtained. The specific surface area of this powder was 25.6m<sup>2</sup>/g, the first [ an average of ] particle size was 0.029 micrometers, and specific resistance (green compact 50 kg/cm<sup>2</sup>) was 60-ohmcm. moreover, the result of the ultrasonic elution test of this powder – Cl:390ppm, In:9ppm, and Sn:7ppm it is – Na and K were not detected. This ITO The color of resin changes at all and was stable, when the high-humidity/temperature trial was performed after kneading and pressing in vinyl resin on the same conditions as an example 1 using powder. Moreover, the paint film with a thickness of 1.2 micrometers was formed with the coating prepared on the same conditions as an example 1 using this ITO powder. The haze value of this paint film was 9.4%, and surface electrical resistance was 2.1x10<sup>4</sup>ohm/\*\*.

[0016] They are NaOH and 250g about example of comparison 1NH<sub>4</sub>HCO<sub>3</sub>. The coprecipitation reaction was carried out like the example 1 except having changed. the last pH at this time – 7.4 it was . Precipitate was succeedingly washed like the example 1, it dried and calcinated, and 220g of ITO powder was obtained. The specific surface area of this powder was 28.1m<sup>2</sup>/g, the first [ an average of ] particle size was 0.029 micrometers, and specific resistance (green compact 50 kg/cm<sup>2</sup>) was 100-ohmcm. Moreover, the result of the ultrasonic elution test of this powder was Cl:0.2wt% and In:0.05wt% and Sn:0.01wt%, and Na was 0.1wt(s)%. After kneading and pressing in vinyl resin on the same conditions as an example 1 using this ITO powder, when the high-humidity/temperature trial was performed, the color of resin was discolored a little green. Moreover, the paint film with a thickness of 1.4 micrometers was formed with the coating prepared on the same conditions as an example 1 using this ITO powder. The haze value of this paint film was 14.6%, and surface electrical resistance was 9.7x10<sup>4</sup>ohm/\*\*.

[0017] They are NaOH and 250g about example of comparison 2NH<sub>4</sub>HCO<sub>3</sub>. The coprecipitation reaction was

carried out like the example 1 except having changed. The last pH at this time was 7.4. Then, precipitate was washed like the example 1, after desiccation, it calcinated at 950 degrees C and 220g of ITO powder was obtained. The specific surface area of this powder was 4cm<sup>2</sup>/g, the first [ an average of ] particle size was 0.25 micrometers, and specific resistance (green compact 50 kg/cm<sup>2</sup>) was 10-ohmcm. Moreover, the result of the ultrasonic elution test of this powder was Cl:0.12wt% and In:0.05wt% and Sn:0.01wt%, and Na was 0.1wt(s)%. When the high-humidity/temperature trial was performed after kneading and pressing in vinyl resin on the same conditions as an example 1 using this ITO powder, the color of resin was discolored a little green. Moreover, the paint film with a thickness of 1.4 micrometers was formed with the coating prepared on the same conditions as an example 1 using this ITO powder. The haze value of this paint film was 22.3%, and surface electrical resistance was 9.7x10<sup>3</sup>ohm/\*\*.

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(54)【発明の名称】 超微粒低抵抗スズドーパ酸化インジウム粉末とその製法

(57)【要約】

【目的】超微粒低抵抗スズドーパ酸化インジウム粉末とその製法を提供する。

【構成】塩化インジウムおよび塩化スズの混合水溶液とアンモニウム炭酸塩とを混合し、温度5℃～95℃、最終pH2～8の条件下でインジウムとスズの水酸化物を共沈させ、該沈殿を加熱分解をすることにより、組成比Sn/Inが0.005～0.3であり、比表面積(BET値)が10m<sup>2</sup>/g以上、比抵抗が70Ωcm以下であって、不純物の塩素が0.1%以下、ナトリウムおよびカリウムが10ppm以下、遊離のインジウムおよびスズが10ppm以下である超微粒低抵抗スズドーパ酸化インジウム粉末(ITO粉末)を得る。

【効果】上記ITO粉末は、粒径が0.08μm以下、好ましくは0.03μm以下の超微粒子であり、しかも比抵抗が70Ωcm以下、好ましくは15Ωcm以下の高導電性を有するので、この粉末を分散させた樹脂や塗料は優れた透明性および導電性を有し、変色などの経時変化のない樹脂や導電性塗膜が得られる。

## 【特許請求の範囲】

【請求項1】 組成比Sn/Inが0.005～0.3であり、比表面積(BET値)が $10\text{m}^2/\text{g}$ 以上、比抵抗が $70\Omega\text{cm}$ 以下であって、不純物の塩素が0.1%以下、ナトリウムおよびカリウムが10ppm以下、遊離のインジウムおよびスズが10ppm以下である超微粒低抵抗スズドーパ酸化インジウム粉末。

【請求項2】 組成比Sn/Inが0.01～0.1であり、比表面積(BET値)が $25\text{m}^2/\text{g}$ 以上、比抵抗が $15\Omega\text{cm}$ 以下である請求項1の超微粒低抵抗スズドーパ酸化インジウム粉末。

【請求項3】 塩化インジウムおよび塩化スズの混合水溶液とアンモニウム炭酸塩との混合によってインジウムとスズの水酸化物を共沈させ、該沈殿を加熱分解することを特徴とする超微粒低抵抗スズドーパ酸化インジウム粉末の製造方法。

【請求項4】 共沈温度が $5^\circ\text{C}$ ～ $95^\circ\text{C}$ であり、共沈反応の最終pHが2～8である請求項3の製造方法。

【請求項5】 加熱分解温度が $400^\circ\text{C}$ ～ $950^\circ\text{C}$ であり、かつ加熱分解時間が30分～8時間である請求項3または4の製造方法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は、比表面積(BET値)が $10\text{m}^2/\text{g}$ 以上、比抵抗が $70\Omega\text{cm}$ 以下、好ましくはBET値が $25\text{m}^2/\text{g}$ 以上、比抵抗が $15\Omega\text{cm}$ 以下である超微粒低抵抗のスズドーパ酸化インジウム(ITO)粉末とその製法に関する。上記ITO粉末は分散性に優れ、この粉末を分散させた塗料は優れた透明性と導電性を有し長時間安定な塗膜を形成できる。

## 【0002】

【従来技術および問題点】 従来、超微粒ITO粉末の一般的な製法としては、水酸化ナトリウム、水酸化カリウム等のアルカリ水溶液を $\text{InCl}_3$ および $\text{SnCl}_4$ の混合水溶液に加えてInとSnの水酸化物を共沈させ、この沈殿を加熱分解して上記ITO粉末を得る方法が知られている。このとき副生した塩化ナトリウムあるいは塩化カリウムは、デカンテーション、遠心分離法等により頻繁に水洗いを繰返して除去し、濾過した沈殿物を乾燥、焼成、粉碎の工程を経て製品化している。上記粉末の粒径は、上記反応温度および焼成温度を制御することにより調整される。またITOの導電機構は、 $\text{In}_2\text{O}_3$ 結晶の3価の $\text{In}^{3+}$ サイトに4価の $\text{Sn}^{4+}$ が置換配置してn形のドナーとして働くことから、ITO粉末の比抵抗は組成比Sn/Inを0.005～0.3の範囲内で調整することによって低抵抗化が行なわれている。

【0003】 しかしながら従来のITO粉末では、第1の問題点として比抵抗(圧粉体 $50\text{kg}/\text{cm}^2$ )が十分に小さい超微粒ITO粉末を得るには限界があった。即ち従来の方法では、沈殿時に副生したNaClあるいはKClが、共沈したInとSnの水酸化物の格子内に取込まれており、デカンテーションあるいは遠心分離法で水洗を十分に行なってもC

I、NaまたはKが少なくともそれぞれ0.05%以上残留するため、これが導電性を障害する要因となり、比抵抗が十分に小さい超微粒ITO粉末は得られていない。特に不純物の塩素は、 $\text{Cl}^-$ イオンとなり $\text{Sn}^{4+}$ イオンの電荷を奪って $\text{Sn}^{3+}$ イオンとし、キャリア電子対を消滅させるので導電性が低下する。さらに不純物塩素は、 $1000^\circ\text{C}$ 以上の高温で強制的に脱離させることができるが、同時にNaやKが0.1%以上共存すると、これらが焼結助剤として作用するため $650^\circ\text{C}$ 以上の温度で著しい粒成長が起こり、粉末が粗粒化するため比抵抗の小さい超微粒ITO粉末を得ることができなくなる。第2の問題点としては、含有する陰イオン $\text{Cl}^-$ は主に陽イオン $\text{Na}^+$ 、 $\text{K}^+$ 、 $\text{In}^{3+}$ および $\text{Sn}^{4+}$ とイオン結合を形成するため、この粉末を樹脂に混合して成形体としたり塗料化した場合、成形体内部や塗膜内部に $\text{Na}^+$ 、 $\text{K}^+$ 、 $\text{In}^{3+}$ 、 $\text{Sn}^{4+}$ および $\text{Cl}^-$ が溶出して樹脂の変色、曇り、劣化等の経時変化を引起し易い問題点があった。

【0004】 【発明の解決課題】 本発明は、従来のITO粉末における上記問題点を解決するものであって、粒径が $0.08\mu\text{m}$ 以下、好ましくは $0.03\mu\text{m}$ 以下の微粒子であり、比抵抗が $70\Omega\text{cm}$ 以下、好ましくは $15\Omega\text{cm}$ 以下の導電性に優れた超微粒ITO粉末とその製法を提供することを目的とする。

## 【0005】

【問題の解決手段：発明の構成】 本発明によれば、組成比Sn/Inが0.005～0.3であり、比表面積(BET値)が $10\text{m}^2/\text{g}$ 以上、比抵抗が $70\Omega\text{cm}$ 以下であって、不純物の塩素が0.1%以下、ナトリウムおよびカリウムが10ppm以下、遊離のインジウムおよびスズが10ppm以下である超微粒低抵抗スズドーパ酸化インジウム粉末が提供される。また本発明によれば、塩化インジウムおよび塩化スズの混合水溶液とアンモニウム炭酸塩との混合によってインジウムとスズの水酸化物を共沈させ、該沈殿を加熱分解することを特徴とする超微粒低抵抗スズドーパ酸化インジウム粉末の製造方法が提供される。

【0006】 本発明のITO粉末は、塩化インジウムおよび塩化スズの混合水溶液とアンモニウム炭酸塩との混合によってインジウムとスズの水酸化物を共沈させ、該沈殿を加熱分解することによって得られる。具体的には、アンモニウム炭酸塩、即ち、炭酸アンモニウム $(\text{NH}_4)_2\text{CO}_3$ 、重炭酸アンモニウム $\text{NH}_4\text{HCO}_3$ 、カルバミン酸アンモニウム $\text{H}_2\text{NCO}_2\text{NH}_4$ の水溶液またはこれらの混合水溶液中に塩化インジウム $\text{InCl}_3$ と塩化スズ $\text{SnCl}_4$ の混合水溶液を滴下することによってインジウムとスズの水酸化物を共沈させ、該沈殿物をデカンテーション又は遠心分離法によって水洗し、乾燥、焼成、粉碎することによって得られる。

【0007】 本発明に用いる $\text{InCl}_3$ 水溶液、 $\text{SnCl}_4$ 水溶液は市販品を用いることができる。一般的な $\text{InCl}_3$ 水溶液および $\text{SnCl}_4$ 水溶液であれば良い。なお $\text{InCl}_3$ 水溶液は金

属In、100重量部を12N-HCl、220～280重量部に溶解して得たものを使用しても良い。InCl<sub>3</sub>水溶液とSnCl<sub>4</sub>水溶液は、粉末での組成比Sn/Clが0.005～0.3となるように混合される。具体的には、InCl<sub>3</sub>、100重量部に対し、SnCl<sub>4</sub>、1～10重量部、好ましくは3～8重量部の範囲に調整される。この範囲を外れると得られたITO粉末の比抵抗が高くなる。

【0008】炭酸塩としては、炭酸アンモニウム(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>、重炭酸アンモニウムNH<sub>4</sub>HCO<sub>3</sub>またはH<sub>2</sub>NCO<sub>2</sub>NH<sub>4</sub>又はこれらの混合物が用いられる。これらの炭酸塩をInCl<sub>3</sub>-SnCl<sub>4</sub>に対して当量から2.5倍当量を使用し、最終pH2～8好ましくは3～6の範囲に調整される。また、最終pHの調整はHCl、HNO<sub>3</sub>、H<sub>2</sub>SO<sub>4</sub>、CH<sub>3</sub>COOH又はこれらの混酸によって所定のpH範囲に調整しても良い。最終pHが2より低い場合には沈殿粒子が再溶解するため好ましくない。また、pHが8を越える場合には沈殿物中の炭酸根が陰イオンのHCO<sub>3</sub><sup>-</sup>あるいはCO<sub>3</sub><sup>2-</sup>として溶解するため、沈殿物を焼成する際に炭酸ガスの脱離が行なわれず、超微粒化と脱塩素化が出来なくなるため好ましくない。本発明においては、上記炭酸塩を用いることにより、共沈したInとSnの水酸化物格子中のOH<sup>-</sup>が部分的にHCO<sub>3</sub><sup>-</sup>またはCO<sub>3</sub><sup>2-</sup>等で置換配置した炭酸塩を含む沈殿を形成させることにより、焼成時に炭酸ガスの脱離によって微粒子化が図られ、かつ比表面積が大きくなるために脱塩素化が容易になる。

【0009】共沈反応の温度は5℃から95℃の範囲内であり、好ましくは10℃から90℃の範囲内である。これより温度が低い場合には沈殿の核生成が不十分であり、かつ収率も低下する。一方、反応温度がこの範囲よりも高い場合には、炭酸が分解し十分に炭酸化が行なわれないため好ましくない。なお低温で沈殿を生成させた後に上記反応温度範囲まで高めても良い。

【0010】上記方法によって生成した沈殿物は、回収後、デカンテーションあるいは遠心分離法等の一般的な洗浄法によって水洗される。最終的には濾液の導電率が2000Ωcm以上になるまで洗浄が行なわれるが、好ましくは5000Ωcm以上になるまで洗浄される。沈殿の導電率がこれより小さい場合には副生したNH<sub>4</sub>Clが充分除去されておらず焼成後のCl含有量が100ppm以上となり、また、溶出性のIn<sup>3+</sup>やSn<sup>4+</sup>がそれぞれ10ppm以上含まれる結果となるため、安定な物性を有するITO粉末を得るのが難しい。

【0011】加熱分解は400℃から950℃の範囲内で30分から8時間の範囲内で焼成され、好ましくは500℃から850℃の範囲内で1時間から6時間の範囲内で焼成される。焼成温度がこの範囲より低い場合にはITOの結晶化が不十分であり、かつ、脱塩素化が不完全となるため比抵抗が15Ωcmよりも大きくなり好ましくない。また、この範囲より焼成温度が高い場合には粒子が粗粒化し、比表面積(BET値)が10m<sup>2</sup>/gよりも小さくなり、粒径が約0.08μm

以上になるので、超微粒子ITO粉末を得るのが難しい。焼成温度が500℃～850℃のとき、粒子の比表面積(BET値)は25m<sup>2</sup>/g以上となり、粒径が約0.03μm以下の超微粒子ITO粉末が得られる。

#### 【0012】実施例1

Inメタル200gを12N-HCl、600ccに加えて完全に溶解させた後、この塩化インジウム溶液にSnCl<sub>4</sub>、60wt%水溶液33gを加えてInCl<sub>3</sub>-SnCl<sub>4</sub>(Sn/In比:0.05)混合溶液を調製した。次に、500gのNH<sub>4</sub>HCO<sub>3</sub>をイオン交換水に溶解し、液量4.5リットル、温度30℃に調整した。この水溶液に上記InCl<sub>3</sub>-SnCl<sub>4</sub>液の全量を約20分間攪拌しながら滴下して沈殿を生成させ、更にそのまま30分間攪拌した。このとき反応液の最終pHは4.5であった。沈殿を回収し、遠心分離機で脱水した後にイオン交換水を加えて洗浄しながら遠心濾過を行い、濾液の導電率が5000Ωcm以上に達したところで遠心濾過を終了した。次いでこの沈殿物を100℃で一晩乾燥した後に600℃で3時間焼成し、粉碎してITO粉末213gを得た。この粉末の比表面積は38.8m<sup>2</sup>/g、平均一次粒径は0.023μmであり、比抵抗(圧粉体50Kg/cm<sup>2</sup>)は1.8Ωcmであった。この粉末1.0gを蒸留水に分散させ、20分超音波振動を与えて溶出成分を分析したところ、Cl:13ppm、In:8ppm、Sn:1ppm以下であり、Na、Kは検出されなかった。次にこのITO粉末2gを塩化ビニル樹脂にヒートロールを用い130℃で混練し、0.3mmにプレスした後に、湿度80%、温度60℃の条件下で20日間放置することにより高温高湿環境下での色の経時変化を試験したところ、樹脂の色は全く変化せず安定であることが確認された。また、このITO粉末12gをポリエステル塗料(樹脂固形分10%)40gに混合したものを容器に入れ、10mmφのアルミナボール100gを用いて20時間攪拌した。その後厚さ75μmのポリエステルフィルムにワイヤバーを用いて塗布し、自然乾燥した後に、90℃、5時間乾燥して厚さ1.2μmの塗膜を形成した。この塗膜のヘーズ値は8.8%であり、表面抵抗は7.6×10<sup>3</sup>Ω/□であった。

#### 【0013】実施例2

実施例1と同様にして調製したInCl<sub>3</sub>溶液に、SnCl<sub>4</sub>、60wt%水溶液200gを加えて、InCl<sub>3</sub>-SnCl<sub>4</sub>(Sn/In比:0.3)混合溶液を調製した。一方、550gの(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>をイオン交換水に溶解して液量9リットル、温度5℃に調整した。該水溶液に上記InCl<sub>3</sub>-SnCl<sub>4</sub>液の全量を攪拌しながら約10分間滴下し、更に塩酸を添加して最終pHを2.0に調整した。この混合溶液を95℃に昇温し30分間熟成した後に、実施例1と同様にして沈殿物を回収し、濾過、乾燥し、400℃で8時間焼成した後に粉碎してITO粉末194gを得た。この粉末の比表面積は72.3m<sup>2</sup>/g、平均一次粒径は0.012μmであり、比抵抗(圧粉体50Kg/cm<sup>2</sup>)は15Ωcmであった。またこの粉末の超音波溶出試験の結果は、Cl:44ppm、In:7ppm、Sn:1ppm以下であり、Na、Kは検出されなかった。このITO粉末を用い、実施例1と同一の条件で、ビニル樹脂に混練してプレスした後に高温高湿試験を行ったとこ

ろ、樹脂の色は全く変化せず安定であった。また、このITO粉末を用い、実施例1と同一の条件で調製した塗料によって、厚さ $1.4\mu\text{m}$ の塗膜を形成した。この塗膜のヘーズ値は8.0%であり、表面抵抗は $9.1\times 10^3\Omega/\square$ であった。

#### 【0014】実施例3

実施例1と同様にして調製した $\text{InCl}_3$ 溶液に、 $\text{SnCl}_4$ 、60wt%水溶液66gを加えて $\text{InCl}_3$ - $\text{SnCl}_4$ (Sn/In比:0.10)混合溶液を調製した。一方、1400gの $\text{NH}_4\text{HCO}_3$ をイオン交換水に溶解して液量9リットル、温度 $95^\circ\text{C}$ に調整した。この水溶液に上記 $\text{InCl}_3$ - $\text{SnCl}_4$ 液の全量を攪拌しながら約10分間滴下し、さらに希塩酸を添加して最終pHを6.0に調整した。その後、実施例1と同様にして沈殿物を回収し、濾過、乾燥し、 $950^\circ\text{C}$ で30分間焼成した後に粉碎してITO粉末217gを得た。この粉末の比表面積は $25.6\text{m}^2/\text{g}$ 、平均一次粒径は $0.029\mu\text{m}$ であり、比抵抗(圧粉体 $50\text{Kg}/\text{cm}^2$ )は $1.3\Omega\text{cm}$ であった。またこの粉末の超音波溶出試験の結果は、Cl:6ppm、InおよびSnは1ppm以下であり、Na、Kは検出されなかった。このITO粉末を用い、実施例1と同一の条件で、ビニル樹脂に混練してプレスした後に高温高湿試験を行ったところ、樹脂の色は全く変化せず安定であった。また、このITO粉末を用い、実施例1と同一の条件で調製した塗料によって、厚さ $1.2\mu\text{m}$ の塗膜を形成した。この塗膜のヘーズ値は9.4%であり、表面抵抗は $7.4\times 10^3\Omega/\square$ であった。

#### 【0015】実施例4

実施例1と同様にして調製した $\text{InCl}_3$ 溶液に、 $\text{SnCl}_4$ 、60wt%水溶液3.3gを加えて、 $\text{InCl}_3$ - $\text{SnCl}_4$ (Sn/In比:0.005)混合溶液を調製した。一方、1400gの $\text{NH}_4\text{HCO}_3$ をイオン交換水に溶解して液量9リットル、温度 $95^\circ\text{C}$ に調整した。この水溶液に上記 $\text{InCl}_3$ - $\text{SnCl}_4$ 液の全量を攪拌しながら約10分間滴下し、更に希塩酸を添加して最終pHを8.0に調整した。その後、実施例1と同様にして沈殿物を回収し、濾過、乾燥し、 $600^\circ\text{C}$ で30分間焼成した後に粉碎してITO粉末230gを得た。この粉末の比表面積は $25.6\text{m}^2/\text{g}$ 、平均一次粒径は $0.029\mu\text{m}$ であり、比抵抗(圧粉体 $50\text{Kg}/\text{cm}^2$ )は $60\Omega\text{cm}$ であった。また、この粉末の超音波溶出試験の結果は、Cl:390ppm、In:9ppm、Sn:7ppmであり、Na、Kは検出されなかった。このITO粉末を用い、実施例1と同一の条件で、ビニル樹脂に混練してプレスした後に高温高湿試験を行ったところ、樹脂の色は全く変化せ

ず安定であった。また、このITO粉末を用い、実施例1と同一の条件で調製した塗料によって、厚さ $1.2\mu\text{m}$ の塗膜を形成した。この塗膜のヘーズ値は9.4%であり、表面抵抗は $2.1\times 10^4\Omega/\square$ であった。

#### 【0016】比較例1

$\text{NH}_4\text{HCO}_3$ をNaOH、250gに変更した以外は実施例1と同様にして共沈反応を実施した。このときの最終pHは7.4であった。引き続き実施例1と同様にして沈殿を洗浄し、乾燥、焼成してITO粉末220gを得た。この粉末の比表面積は $28.1\text{m}^2/\text{g}$ 、平均一次粒径は $0.029\mu\text{m}$ であり、比抵抗(圧粉体 $50\text{Kg}/\text{cm}^2$ )は $100\Omega\text{cm}$ であった。また、この粉末の超音波溶出試験の結果は、Cl:0.2wt%、In:0.05wt%、Sn:0.01wt%、Naは0.1wt%であった。このITO粉末を用い、実施例1と同一の条件で、ビニル樹脂に混練してプレスした後に、高温高湿試験を行ったところ、樹脂の色はやや緑色に変色した。またこのITO粉末を用い、実施例1と同一の条件で調製した塗料によって厚さ $1.4\mu\text{m}$ の塗膜を形成した。この塗膜のヘーズ値は14.6%であり、表面抵抗は $9.7\times 10^4\Omega/\square$ であった。

#### 【0017】比較例2

$\text{NH}_4\text{HCO}_3$ をNaOH、250gに変更した以外は実施例1と同様にして共沈反応を実施した。このときの最終pHは7.4であった。引き続き、実施例1と同様にして沈殿を洗浄し、乾燥後、 $950^\circ\text{C}$ で焼成してITO粉末220gを得た。この粉末の比表面積は $4\text{cm}^2/\text{g}$ 、平均一次粒径は $0.25\mu\text{m}$ であり、比抵抗(圧粉体 $50\text{Kg}/\text{cm}^2$ )は $10\Omega\text{cm}$ であった。またこの粉末の超音波溶出試験の結果は、Cl:0.12wt%、In:0.05wt%、Sn:0.01wt%、Naは0.1wt%であった。このITO粉末を用い、実施例1と同一の条件で、ビニル樹脂に混練してプレスした後に高温高湿試験を行ったところ、樹脂の色はやや緑色に変色した。またこのITO粉末を用い、実施例1と同一の条件で調製した塗料によって、厚さ $1.4\mu\text{m}$ の塗膜を形成した。この塗膜のヘーズ値は22.3%であり、表面抵抗は $9.7\times 10^3\Omega/\square$ であった。

#### 【0018】

【発明の効果】本発明のITO粉末は、比表面積(BET値)が $10\text{m}^2/\text{g}$ 以上、比抵抗が $70\Omega\text{cm}$ 以下、好ましくは比表面積(BET値)が $25\text{m}^2/\text{g}$ 以上、比抵抗が $15\Omega\text{cm}$ 以下であり、この粉末を分散させた樹脂や塗料は優れた透明性および導電性を有し、変色などの経時変化のない樹脂や導電性塗膜が得られる。